

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-336152

(43)Date of publication of application : 05.12.2000

(51)Int.Cl.

C08G 61/08

(21)Application number : 11-150558

(71)Applicant : HITACHI CHEM CO LTD

(22)Date of filing : 28.05.1999

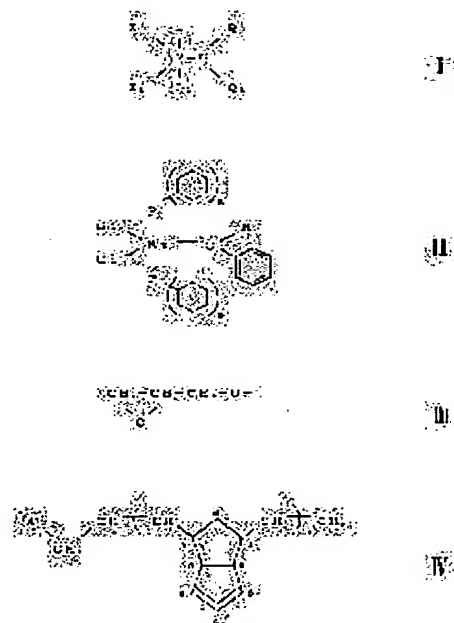
(72)Inventor : KIKUCHI NOBURU  
 AIHARA AKIO  
 KAWAI HIROMASA  
 KATOI SHIGEKI

## (54) DICYCLOPENTADIENE RING-OPENED POLYMER HAVING FUNCTIONAL GROUP AT ONE END AND ITS PRODUCTION

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To obtain the subject polymer at whose one end has a functional group capable of imparting a function such as reactivity, radical polymerizability, flame retardancy and adhesivity to various urachine parts, by subjecting dicyclopentadiene to a ring-opening polymerization in the presence of a specific catalyst and a specific chain transfer agent.

**SOLUTION:** A polymer of formula IV [(n) is 1 to 50 on the average; a double bond is disposed between the No.3 carbon and the No.4 carbon or between the No.4 carbon and the No.5 carbon] is obtained by subjecting dicyclopentadiene to a ring-opening metathesis polymerization in the presence of a compound of formula I (M is ruthenium or osmium; X, X1 are each an anionic ligand; L, L1 are each a neutral electron donor group; Q, Q1 are each H or an alkyl, alkenyl or aromatic group which may have a substituent) (for example, a ruthenium carbene complex of formula II) as a catalyst and an allyl compound of the formula: X-CH2-CH=CH2 [X is a group of formula III or a group of the formula: (CH3CH3O)3-Si- or the like] (for example, allylglycidyl ether) as a chain transfer agent.



## LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

**BEST AVAILABLE COPY**

Copyright (C); 1998,2003 Japan Patent Office

---

JPO and NCIP are not responsible for any damages caused by the use of this translation.

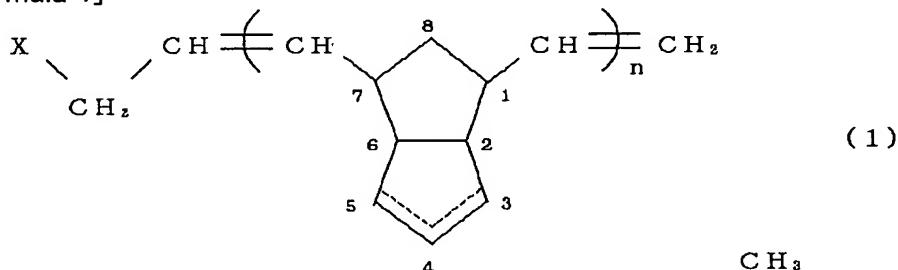
- 1.This document has been translated by computer. So the translation may not reflect the original precisely.  
2.\*\*\*\* shows the word which can not be translated.  
3.In the drawings, any words are not translated.

## CLAIMS

**[Claim(s)]**


[Claim 1] The polymer shown by the general formula [1].

[Formula 1]



ここで、Xは  $\text{CH}_2-\underset{\text{O}}{\underset{|}{\text{CH}}}-\text{CH}_2-\text{O}-$  又は  $\text{CH}_2=\underset{\text{O}}{\underset{||}{\text{C}}}-\text{C}-\text{O}-$

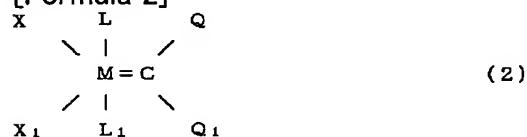
又は  $(\text{CH}_3\text{CH}_2\text{O})_3\text{Si}-$  又は

又は  $\text{CH}_3\text{CH}_2\text{CH}_2\text{O}-$  又は 

It comes out, and it is the functional group shown and between 3 and 4 is [ n averages, and is 1–50 and / between double association or the carbon numbers 4 and 5 ] double association in the carbon number shown in Arabic numerals.

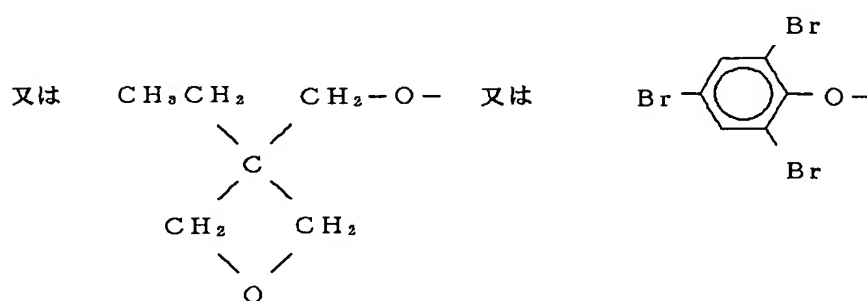
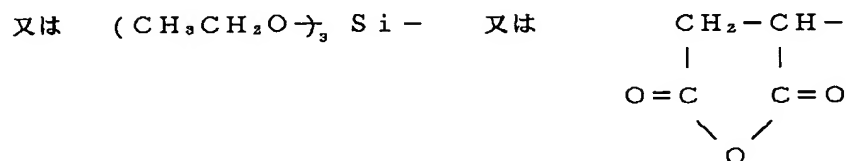
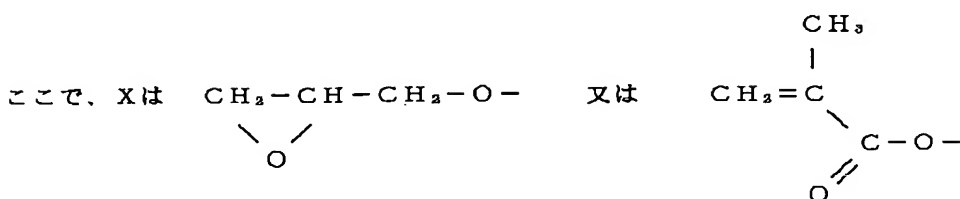
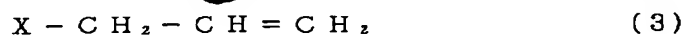
[Claim 2] The compound shown by the general formula [2] considering a dicyclopentadiene as a catalyst,

[Formula 2]



(M may show a ruthenium or an osmium, and the electron donative group of neutrality [1 / an anionic ligand, and / L and L1 / 1 / X and / X], Q and Q1 may show hydrogen, an alkyl group, an alkenyl radical, or an aromatic series radical independently, respectively, and the alkyl group, the alkenyl radical, or the aromatic series radical

may have the substituent.) And the vinyl compound shown by the general formula [3] as a chain transfer agent  
 [\*\* 3]



The manufacturing method of the polymer according to claim 1 characterized by carrying out a ring opening methathesis under \*\*\*\*\*.

[Translation done.]

## \*NOTICES\*

JPO and NCIP are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

DETAILED DESCRIPTION

---

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach with the polymer which has the functional group obtained by carrying out metathesis ring opening polymerization of the dicyclopentadiene at the piece end. It is related with the metathesis ring-opening-polymerization object of the dicyclopentadiene which can give functions to reactivity, radical polymerization nature, fire retardancy, and various base materials more useful to the property improvement of the polymer ingredient of various kinds [ detail ], such as an adhesive property.

[0002]

[Description of the Prior Art] The method of carrying out metathesis ring opening polymerization of the dicyclopentadiene, and obtaining a polymer is learned from ancient times. for example, JP,53-24400,A -- setting -- as a tungsten catalyst and an activator -- the [ from the Ith group of the periodic table ] -- the approach of compounding using chain-like olefin compounds, such as 1-hexene, 1-octene, styrene, a vinyl chloride, and vinyl ether, as a chain transfer agent (molecular-weight modifier) is indicated using the catalyst system which changes combining the organometallic compound to IV group.

[0003] Moreover, in Polymer Journal, Vol 27, No.12, and pp 1167-1172 (1995), 1-hexene is used for the bottom of existence of the catalyst system which changes combining tetramethyl tin as tungsten hexachloride and an activator as a chain transfer agent, and number average molecular weight is  $1.12 \times 10^4$ . The method of obtaining the ring breakage linear polymer of a dicyclopentadiene is described.

[0004] Thus, although the ring breakage linear polymer of the dicyclopentadiene by which molecular weight was controlled by using a chain transfer agent was obtained, with an old technique, the compound used for a chain transfer agent is a chain-like olefin compound without a functional group, and was not able to use the compound which has a functional group as a chain transfer agent. The catalyst system which combined the used catalyst component and the activator reacted easily with water, air (oxygen), and various kinds of functional groups, and the reason was for deactivating. Therefore, since the ring breakage linear polymer of the dicyclopentadiene which uses a chain-like olefin compound without a functional group for a chain transfer agent, and is obtained was the so-called hydrocarbon resin without a functional group, the application was restricted.

[0005]

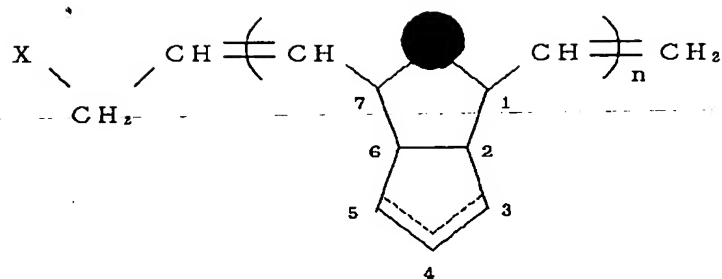
[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the metathesis ring-opening-polymerization object of the dicyclopentadiene which has the functional group which can give functions, such as reactivity, radical polymerization nature, fire retardancy, and an adhesive property to various equipments, at the piece end. That is, a piece end is provided with a glycidyl ether radical, a methacryloyl radical, an acid-anhydride radical, alkoxysilane, TORIBUROMO phenyl ether, and the metathesis ring-opening-polymerization object of the dicyclopentadiene which has the functional group of oxetane.

[0006]

[Means for Solving the Problem] In carrying out metathesis ring opening polymerization of the dicyclopentadiene, this invention acquires the ring-opening-polymerization object of the dicyclopentadiene which molecular weight is controlled and has a functional group at the piece end by using the allyl compound which has a functional group under the carbene complex catalyst existence of a ruthenium or an osmium. The polymer of this invention is a polymer shown by the general formula [1].

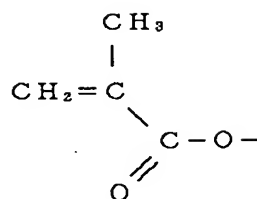
[0007]

[Formula 4]

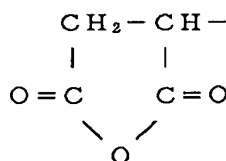


(1)

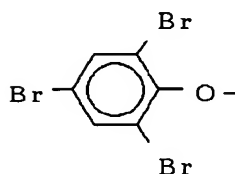
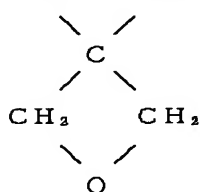
ここで、Xは  $\text{CH}_2-\text{CH}-\text{CH}_2-\text{O}-$  又は



又は  $(\text{CH}_3\text{CH}_2\text{O})_3\text{Si}-$  又は

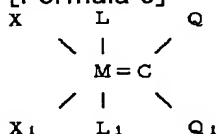


又は  $\text{CH}_3\text{CH}_2-\text{CH}_2-\text{O}-$  又は



It comes out, and it is the functional group shown and between 3 and 4 is [ n averages, and is 1-50 and / between double association or the carbon numbers 4 and 5 ] double association in the carbon number shown in Arabic numerals. Manufacture of the polymer of this invention is the compound shown by the general formula [2] considering a dicyclopentadiene as a catalyst, and [0008].

[Formula 5]



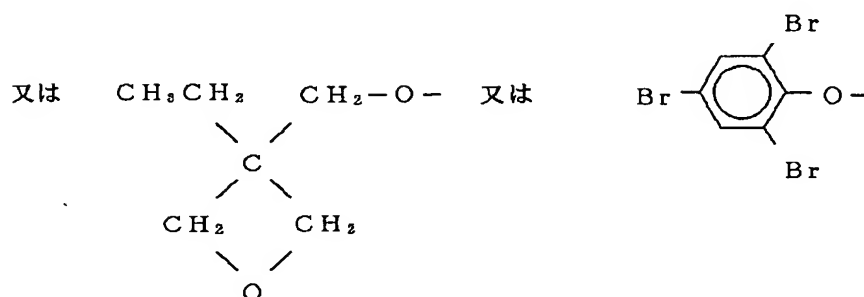
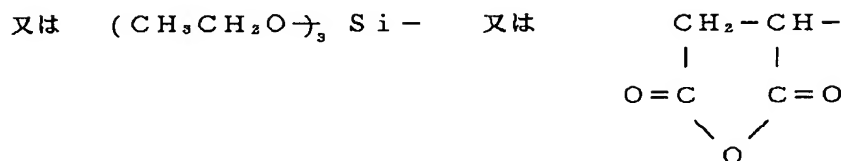
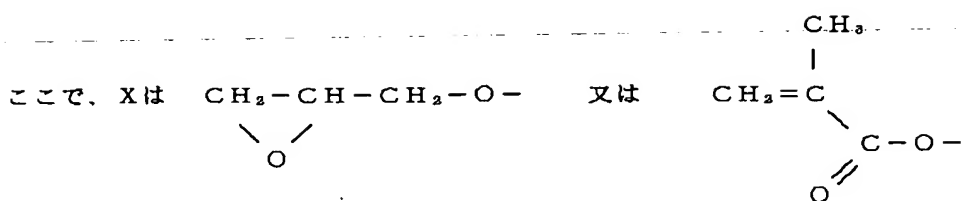
(2)

(M may show a ruthenium or an osmium, and the electron donative group of neutrality [1 / an anionic ligand, and / L and L1 / 1 / X and / X], Q and Q1 may show hydrogen, an alkyl group, an alkenyl radical, or an aromatic series radical independently, respectively, and the alkyl group, the alkenyl radical, or the aromatic series radical may have the substituent.) And the allyl compound shown by the general formula [3] as a chain transfer agent [0009]

[Formula 6]



(3)



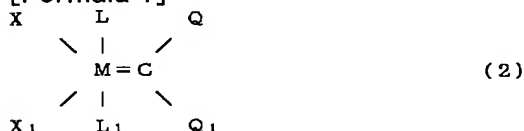
It is characterized by carrying out a ring opening metathesis under \*\*\*\*\*.

[0010]

[Embodiment of the Invention] The metathesis polymerization catalyst which can be used in this invention is a catalyst to which metathesis ring opening polymerization of the dicyclopentadiene can be carried out with the allyl compound which has oxygen, moisture, and functional group in air unlike the catalyst which combined a catalyst component which is known conventionally, and the activator, without losing catalytic activity. A thing desirable as such a metathesis polymerization catalyst is a general formula [2].

[0011]

[Formula 7]



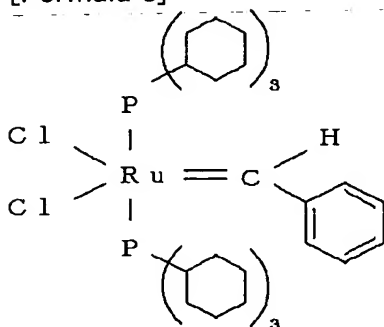
In a general formula [2], M shows a ruthenium or an osmium. X and X1 An anionic ligand is shown independently, respectively. An anion ligand is a radical with an electronegative charge, when the coordination to a central metal is removed. As such a radical, for example Hydrogen, a halogen, and CF<sub>3</sub> CO<sub>2</sub>, CH<sub>3</sub> CO<sub>2</sub>, CFH<sub>2</sub> CO<sub>2</sub>, 3 (CH<sub>3</sub>) CO, 2 (CF<sub>3</sub>) CO (CH<sub>3</sub>), (CF<sub>3</sub>) There are 2CO, the alkyl group of carbon numbers 1-5, the alkoxy group of carbon numbers 1-5, a phenyl group, a phenoxy group, a tosyl group, a mesyl radical, a trifluoromethane sulfonate radical, etc., and both of especially a desirable thing are halogens (especially chlorine) (CH<sub>3</sub>). L and L1 A neutral electron donative group is shown independently, respectively. A neutral electron donative group is having a neutral charge, when the coordination to a central metal is removed. as such a radical -- PR two R<sub>3</sub>R<sub>4</sub> (here -- it is -- R<sub>2</sub> -- the alkyl group of the 2nd class, or a cycloalkyl substrate --) R<sub>3</sub> And R<sub>4</sub> An aryl group, the 1st class alkyl group of carbon numbers 1-10 or the 2nd class alkyl group, and a cycloalkyl radical are shown independently, respectively. There are a phosphine system electron donative group expressed, a pyridine, p-fluoro pyridine, an imidazo RIRIDEN compound, etc. especially a desirable thing L and L1 both - P(cyclohexyl) 3, -P(cyclopentyl) 3, or -P(isopropyl) 3 it is -- it is a thing. Moreover, L and L1 You may differ mutually. Q and Q1 Hydrogen, an alkyl group, an alkenyl radical, or an aromatic series radical is shown independently, respectively. As an alkyl group, there is an aryl group etc. as the alkyl group of carbon numbers 1-20, and an alkenyl radical as the alkenyl radical of carbon numbers 2-20, and an aromatic series radical, and said alkyl group, the alkenyl radical, or the aromatic series radical may have the substituent.

[0012] The concrete thing of the compound (catalyst) shown by the general formula [2] is the ruthenium carbene

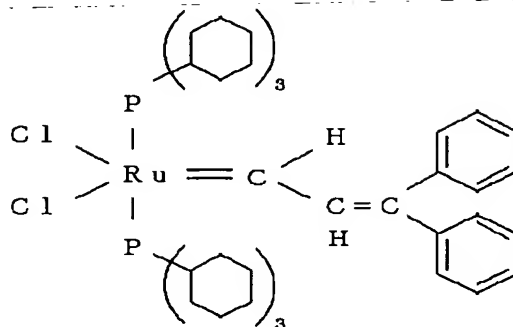
complex which is mentioned to for example, formula (a) - (f).

[0013]

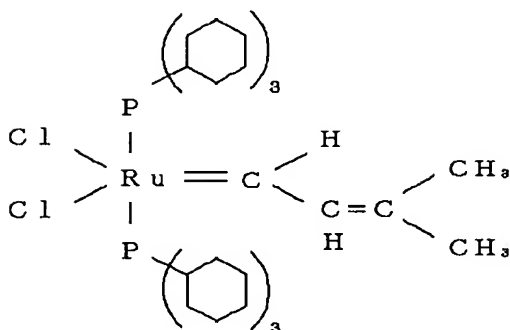
[Formula 8]



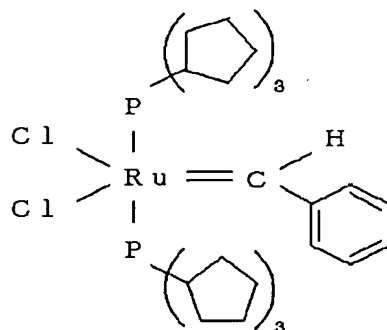
(a)



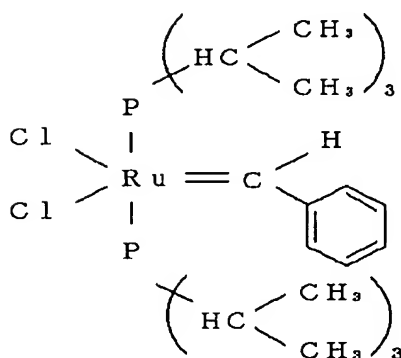
(b)



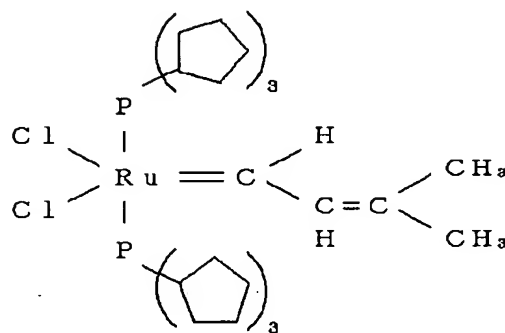
(c)



(d)



(e)



(f)

[0014] The synthesis method of the above-mentioned compound (catalyst) is Journal of American Chemical Society. 3867 pages (1997) No. 18 is further shown in the 16th volume of Organometallics, No. 18, and 4001 pages (1997) the 118th volume, 100 pages (1996), or the 16th volume of Organometallics.

[0015] A commercial dicyclopentadiene can be used for the dicyclopentadiene used for this invention. Although the dicyclopentadiene by which usual is marketed may contain vinyl norbornene, a tetrahydro indene, methylvinyl norbornene, a methyl tetrahydro indene, a methyl dicyclopentadiene, a dimethyl dicyclopentadiene, tricyclopentadiene, etc. as an impurity, these can be contained in the range which does not spoil the purpose of this invention. Usually, the dicyclopentadiene to be used is the thing of 90% of the weight or more of purity, and is the thing of 97% of the weight or more of purity preferably.

[0016] The following are mentioned to the allyl compound which has the functional group used as a chain transfer agent by this invention. Allyl glycidyl ether, allyl compound methacrylate, allyl compound - 2, 4, 6-TORIBUROMO phenyl ether, allyl compound triethoxysilane, an allyl compound succinic-acid anhydride, 3-allyloxy methyl-3-ethyl oxetane. Each of these is marketed as heavy chemicals or a reagent, and can be used as



they are.

[0017] The mole ratio ([dicyclopentadiene] / [an allyl compound]) of a dicyclopentadiene and the allyl compound which has the functional group used as a chain transfer agent specifies  $n$  in a general formula [1] directly. That is, the molecular weight of a polymer will be controlled. Although  $n$  is changed by the purpose of using a polymer, as for the polymer of this invention,  $n$  prepares an allyl compound so that 1–50, i.e., a mole ratio, may turn into 1–50. When a mole ratio is 50 or more, the rate of the end functional group occupied in the polymer obtained becomes small, and functions, such as an adhesive property and fire retardancy, are hard coming to be discovered and are not desirable.

[0018] Let the amount of the catalyst used be a complement advancing a reaction. Although it changes according to the class of catalyst, it is usually 0.01 – 1 weight section preferably to the dicyclopentadiene 100 weight section from the reason of 0.001 – 5 weight section, economical efficiency, and the degree of reaction ream.

[0019] Although it may be able to compound without  $n$ 's [ in / in the polymer which it is going to manufacture / a general formula [1] ] averaging, and using a solvent if it is 1 or about two oligomer, usually the metathesis ring-opening-polymerization reaction of a dicyclopentadiene is not blocked, the dicyclopentadiene of a raw material, an allyl compound, and the polymer to generate are dissolved, and an inactive solvent is used for these. As a solvent used, halogen system solvents, such as ketone system solvents, such as cycloalkane system solvents, such as aromatic series solvents, such as toluene, a xylene, ethylbenzene, and a tetralin, a cyclohexane, cycloheptane, and cyclooctane, an acetone, a methyl ethyl ketone, and a cyclohexanone, dichloromethane, and chloroform, are mentioned.

[0020] Although it changes also with the molecular weight of the polymer which it is going to manufacture, the amount of the solvent to be used is used so that the concentration of a substrate may usually become 5 – 70% of the weight.

[0021] Although a reaction advances also under air, as for the ambient atmosphere at the time of polymer manufacture, it is desirable to make it an inert atmosphere with nitrogen, an argon, etc.

[0022] The reaction temperature for polymer manufacture is 0–100 degrees C, and is 60 degrees C from a room temperature (20 degrees C) preferably. A reaction becomes late and is not realistic although at least 0 degree C or less of reactions advances. Moreover, in the case of 100 degrees C or more, it falls and is not desirable [ yield ] in order that the three-dimension bridge formation object of a dicyclopentadiene may carry out a byproduction. Since the NOBORUNEN ring of a dicyclopentadiene carries out ring breakage and the strain energy of a ring is emitted, this reaction is exothermic reaction. Therefore, it is desirable to cool suitably and to control reaction temperature.

[0023] Although reaction time changes with the amount of catalysts, and reaction temperature, it is usually 15 minutes – 10 hours. It is desirable to react until the dicyclopentadiene of a raw material consumes by the reaction.

[0024] (The reaction halt approach) Although a polymerization reaction will stop automatically if the dicyclopentadiene of a raw material reacts and is consumed, only the number of mols as a catalyst with the same polymer molecule in the condition that the catalyst was attached exists in the piece end opposite to the piece end to which the functional group of a polymer is attached. Since a polymer may color [ that a catalyst is attached to a polymer end, and ] or polymers may gel in response to the time of condensing the solution which the polymer is dissolving, it is desirable to separate a catalyst from a polymer. It can attain by adding to an excess as an approach of separating a catalyst from a polymer from the number of mols of the catalyst which used vinyl compounds, such as ethyl vinyl ether and acetic-acid vinyl ester.

[0025] (After treatment) It is the approach of slushing reaction mixture into poor solvents, such as  $n$ -hexane, a methanol, and water, reprecipitating a polymer, and drying a powder-like polymer after completing a reaction and separating a catalyst from a polymer. Or a polymer can be obtained by removing a solvent for reaction mixture using a film evaporator. Moreover, it is possible to also make it denaturalize and react to the ingredient made into the following purpose, with a solvent existed.

[0026] (Additive; polymerization inhibitor) It is desirable to use allyl compound methacrylate for a chain transfer agent, and to add polymerization inhibitor to the system of reaction, in order to control the polymerization of a methacryloyl radical in case the polymer of the structure which the methacryloyl radical added to the piece end is obtained. As polymerization inhibitor, it is 4-methoxyphenol generally used, and the amount is 10–1,000 ppm of a polymer.

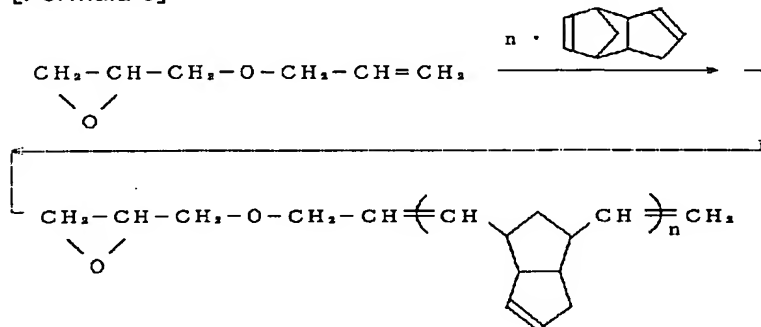
[0027] (Additive; anti-oxidant) Since the obtained polymer has the double bond which the dicyclopentadiene of a raw material has, and the double bond of tales doses, it may oxidize and may generate the gel state. For this reason, it is desirable to add an antioxidant to the system of reaction. As an antioxidant used, if there is antioxidizing ability, there will be especially no limit. The antioxidant of a hindered phenol system is desirable.

2,6-di-tert-butyl-4-methylphenol, 2,4-di-tert-butyl-4-ethylphenol, Stearyl-bet, 3,5-G t-butyl-4-hydroxyphenyl) propionate, Tetrakis-[methylene-3,3',5'-G t-butyl-4'-hydroxyphenyl) propionate] methane, 2 and 2'-methylenebis (4-methyl-6-t-butylphenol), 2 and 2'-methylenebis (4-ethyl-6-t-butylphenol), 4 and 4'-methylenebis (2,6-G t-butylphenol), 1 and 3,5-trimethyl-2,4,6-tris (3,5-G t-butyl-4-hydroxybenzyl) benzene, 1,3,5-tris (3',5'-G t-butyl-4'-hydroxybenzyl)-s-triazine-2,4,6-(1H,3H,5H) trione etc. is mentioned. The addition of an antioxidant is usually 10-10,000 ppm.

[0028]

[Example] Composition of an example 1 glycidyl-ether end polymer [0029]

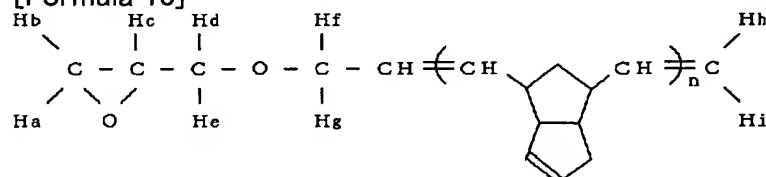
[Formula 9]



Toluene 293.5g, dicyclopentadiene of 99% of purity 250.61g (1.896 mols), and allyl-glycidyl-ether 43.93g (0.385 mols) were taught to 1l. separable flask which attached an agitator, a thermometer, nitrogen gas installation tubing, and an Alin Mr. condensator (mole-ratio = a [dicyclopentadiene] / [allyl-glycidyl-ether] =4.93, substrate concentration = 50.1%), and the inside of a flask was cooled to 5 degrees C by the ice bath, carrying out 0.1 l/min circulation of the nitrogen gas. After removing an ice bath, 0.210g (it is the 0.0838 weight section to 2.55xten - four mols and the dicyclopentadiene 100 weight section) was added for the screw (tri-cyclohexyl phosphine) Ben Jiri Jean ruthenium dichloride shown by the formula (a) as a catalyst. Since the temperature in a flask rose and the inside of a flask amounted to 45 degrees C after [ of reaction initiation ] 20 minutes while adding the catalyst, the inside of a flask was kept at 45 degrees C by the ice bath. The temperature in a flask began to descend after [ of an after / reaction initiation ] 40 minutes, and it became 25 degrees C in 120 minutes after reaction initiation. In order to separate a catalyst from a polymer, 1.74g (0.020 mols) was added for acetic-acid vinyl ester, and churning was continued for 15 minutes. After reaction termination, after removing muddiness of a minute amount by filtration actuation, toluene was distilled off by the rotary evaporator and 277g of wax-like polymers was obtained. Yield was 94%. The GPC analysis result about this polymer is shown in drawing 1 . The number average molecular weight Mn of this polymer by polystyrene conversion was 748, and n was an average of 4.8. Moreover, weight average molecular weight Mw was 1,538, and degree of dispersion (Mw/Mn) of a polymer was 2.06. Moreover, the proton nuclear-magnetic-resonance spectrum (1 H-NMR) of this polymer is shown in drawing 2 . The peak (integral value: 180.88) of the proton combined with the internal double bond is observed at the peak (integral value: 19.66) based on Hh and Hi, and 5.20-6.00 ppm at the peak (integral value: 8.95) based on Hd of the following formula to 3.35-3.45 ppm, the peak (integral value: 8.49) based on helium to 3.65-3.75 ppm, and 4.93-5.07 ppm. By analyzing this result, a glycidyl ether radical exists in the piece end of a polymer, and it is checked that n of the following type is the polymer of 4.9.

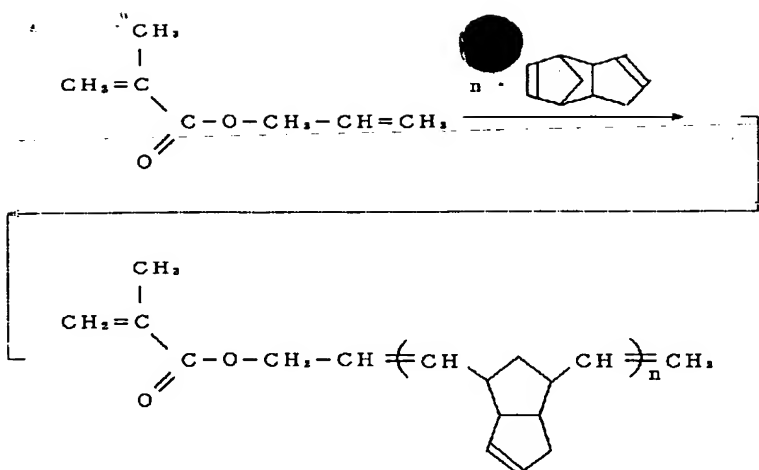
[0030]

[Formula 10]



[0031] Composition of an example 2 methacryloyl end polymer [0032]

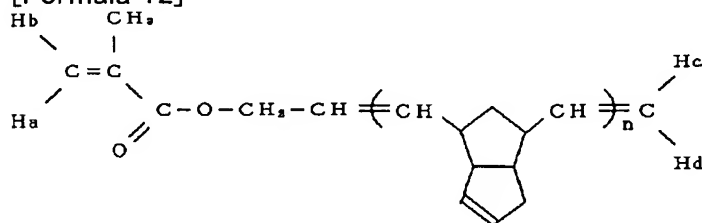
[Formula 11]



To 1l. separable flask which attached an agitator, a thermometer, nitrogen gas installation tubing, and an Alin Mr. condenser Toluene 275.7g, dicyclopentadiene of 99% of purity 231.55g (1.752 mols), Allyl compound methacrylate 44.19g (0.3503 mols) and the antioxidant 2 with which 250 ppm of polymerization inhibitor 4-methoxyphenol are added, 6-JITA challs butyl-4-methyl phenol 14mg was taught (mole-ratio = a [dicyclopentadiene] / [allyl compound methacrylate] = 5.00, substrate concentration = 50.0%), and the inside of a flask was cooled to 6 degrees C by the ice bath, carrying out 0.1l. / min circulation of the nitrogen gas. After removing an ice bath, 0.197g (it is the 0.0851 weight section to 2.39xten - four mols and the dicyclopentadiene 100 weight section) was added for the screw (tri-cyclohexyl phosphine) Ben Jiri Jean ruthenium dichloride shown by the formula (a) as a catalyst. Since the temperature in a flask rose and the inside of a flask amounted to 40 degrees C after [ of reaction initiation ] 15 minutes while adding the catalyst, the inside of a flask was kept at 40 degrees C by the ice bath. The temperature in a flask began to descend after [ of an after / reaction initiation ] 50 minutes, and it became 27 degrees C in 120 minutes after reaction initiation. In order to separate a catalyst from a polymer, 1.74g (0.020 mols) was added for acetic-acid vinyl ester, and churning was continued for 15 minutes. After reaction termination, after removing muddiness of a minute amount by filtration actuation, the toluene of a solvent was distilled off using the rotary evaporator and 262g of wax-like polymers was obtained. Yield was 95%. The GPC analysis result of this polymer is shown in drawing 3 . The number average molecular weight Mn of this polymer by polystyrene conversion was 782, and n was an average of 4.96. Moreover, weight average molecular weight Mw was 1,446, and degree of dispersion (Mw/Mn) of a polymer was 1.85. Moreover, the proton nuclear-magnetic-resonance spectrum (1 H-NMR) of this polymer is shown in drawing 4 . The peak (integral value: 231.7) of the proton combined with the internal double bond is observed at the peak (integral value: 22.1) based on the end olefin of Hc and Hd of the following formula, and 5.23-6.00 ppm at the peak (integral value: 31.5) based on the methyl group of a methacryloyl radical to 1.95 ppm, the peak (integral value: 11.4) based on Ha of the following formula to 6.13 ppm, and 4.90-5.07 ppm. By analyzing this result, a methacryloyl radical exists in the piece end of a polymer, and it is checked that n of the following type is the polymer of 5.0.

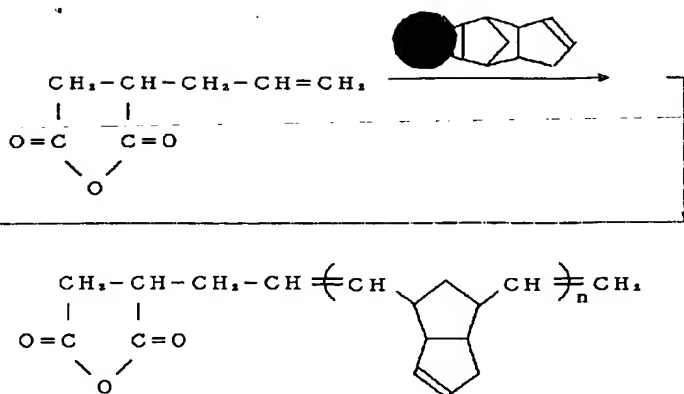
[0033]

[Formula 12]



[0034] Composition of an example 3 acid-anhydride end polymer [0035]

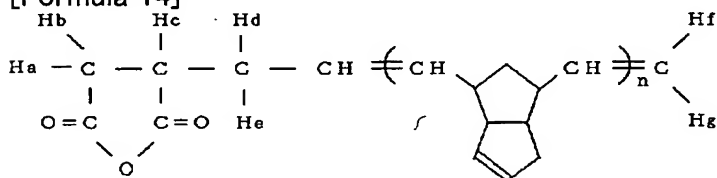
[Formula 13]



a thermometer and electromagnetism -- taught toluene 12.12g, dicyclopentadiene of 99% of purity 10.01g (75.7mmol), and 2.20g (15.7mmol) of anhydrous allyl compound succinic acids to 100ml 3 Thu opening flask which attached the rotator, and it was made to agitate at a room temperature (20 degrees C), and considered as the homogeneity solution. 8.8mg (1.07x10<sup>-5</sup> mol) was added for the screw (tri-cyclohexyl phosphine) Ben Jiri Jean ruthenium dichloride shown in this by the formula (a) as a catalyst. While adding the catalyst, the temperature in a flask rose, and the inside of a flask amounted to 50 degrees C after [ of reaction initiation ] 6 minutes. The temperature in a flask fell gradually after this, and the temperature in a flask became 22 degrees C in 60 minutes after reaction initiation. At this time, 0.27g (3.1mmol) of acetic-acid vinyl ester was added, and it was agitated for 15 minutes. After reaction termination, after removing muddiness of a minute amount by filtration actuation, toluene was distilled off by the rotary evaporator and 11.23g of wax-like polymers was obtained. Yield was 92%. The GPC analysis result of this polymer is shown in drawing 5 . The number average molecular weight Mn of this polymer by polystyrene conversion was 780, and n was an average of 4.84. Moreover, weight average molecular weight Mw was 2,483, and degree of dispersion (Mw/Mn) of a polymer was 3.18. Next, the proton nuclear-magnetic-resonance spectrum (1 H-NMR) of this polymer is shown in drawing 6 . The peak (integral value: 263.9) of the proton combined with the internal double bond at the peak (integral value: 20.2) based on the end olefin of Hf and Hg of the following type and 5.15-6.00 ppm is observed by 4.90-5.07 ppm. By analyzing this result, it is checked that n of the following type is the polymer of 6.28.

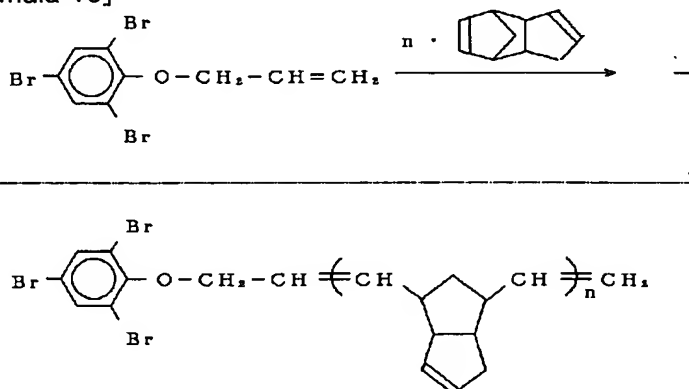
[0036]

[Formula 14]



[0037] Composition of an example 4 TORIBUROMO phenyl ether end polymer [0038]

[Formula 15]

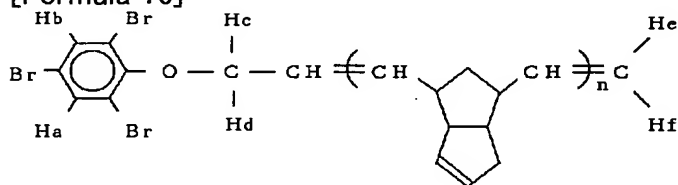


a thermometer and electromagnetism -- 100ml 3 Thu opening flask which attached the rotator -- toluene 15.61g, dicyclopentadiene of 99% of purity 10.01g (75.7mmol), and allyl compound - taught 2, 4, and 6-TORIBUROMO phenyl ether 5.62g (15.2mmol), and it was made to agitate at a room temperature (22 degrees C), and considered as the homogeneity solution. 9.1mg (1.11x10<sup>-5</sup> mol) was added for the screw (tri-cyclohexyl phosphine) Ben Jiri Jean ruthenium dichloride shown by the formula (a) as a catalyst to this. While adding the

catalyst, the temperature in a flask rose, and it amounted to 44 degrees C after [ of reaction initiation ] 7 minutes. The temperature in a flask fell gradually after this, and the inside of a flask became 23 degrees C in 60 minutes after reaction initiation. At this time, 0.27g (3.1mmol) of acetic-acid vinyl ester was added, and churning was carried out for 15 minutes. After reaction termination, after removing muddiness of a minute amount by filtration actuation, toluene was distilled off by the rotary evaporator and 13.13g of wax-like polymers was obtained. Yield was 84%. The GPC analysis result of this polymer is shown in drawing 7. The number average molecular weight Mn of this polymer by polystyrene conversion was 586, and n was an average of 1.63. Moreover, weight average molecular weight Mw was 1,333, and degree of dispersion (Mw/Mn) of a polymer was 2.27. Next, the proton nuclear-magnetic-resonance spectrum (1 H-NMR) of this polymer is shown in drawing 8. The peak (integral value: 337.4) of the proton combined with the internal double bond is observed at the peak (integral value: 36.0) based on the end olefin of helium and Hf of the following formula, and 5.23–6.00 ppm at the peak (integral value: 18.4) based on Ha and Hb of the following formula to 7.64 ppm, the peak (integral value: 41.0) based on Hc and Hd to 4.45–4.72 ppm, and 4.90–5.07 ppm. By analyzing this result, TORIBUROMO phenyl ether exists in the piece end of a polymer, and it is checked that n of the following type is the polymer of 3.9.

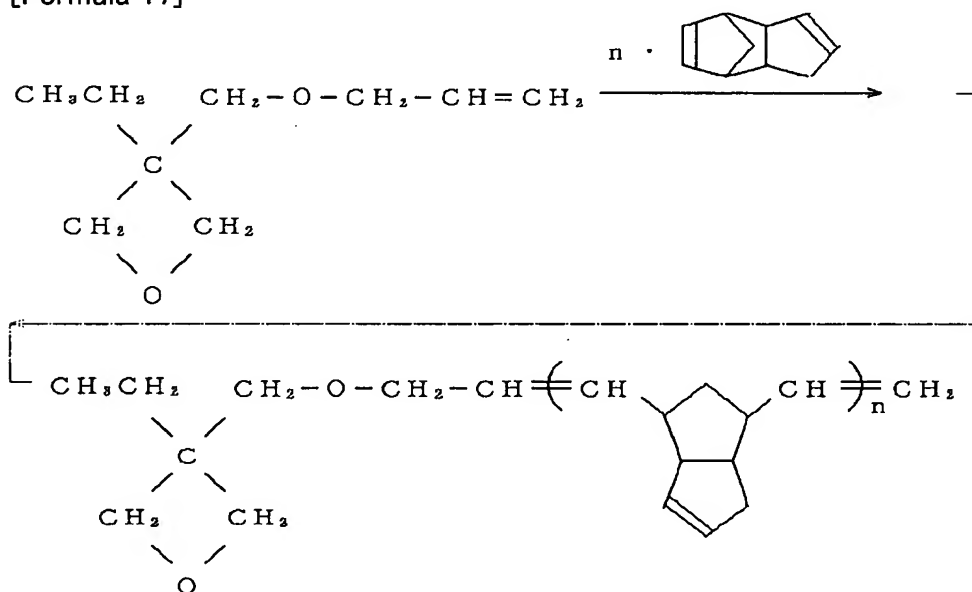
[0039]

[Formula 16]



[0040] Composition of an example 5 oxetane end polymer [0041]

[Formula 17]

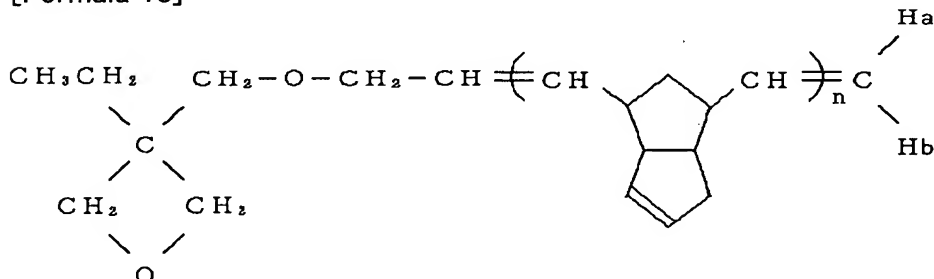


a thermometer and electromagnetism -- toluene 12.42g, dicyclopentadiene of 99% of purity 10.01g (75.7mmol), and 3-allyloxy methyl-3-ethyl oxetane 2.38g (15.2mmol) were taught to 100ml 3 Thu opening flask which attached the rotator, and it agitated at the room temperature (24 degrees C) (mole-ratio = a [dicyclopentadiene] / [3-allyloxy methyl-3-ethyl oxetane] = 4.97, substrate concentration = 49.9%), and considered as the homogeneity solution. 52.6mg (it is the 0.525 weight section to 6.39x10 to 5 mol and the dicyclopentadiene 100 weight section) was added for the screw (tri-cyclohexyl phosphine) Ben Jiri Jean ruthenium dichloride shown by the formula (a) as a catalyst to this. While adding the catalyst, the temperature in a flask rose, and it amounted to 65 degrees C after [ of reaction initiation ] 4 minutes. The temperature in a flask fell gradually after this, and the inside of a flask became 27 degrees C in 40 minutes after reaction initiation. At this time, 1.36g (15.8mmol) of acetic-acid vinyl ester was added, and churning was carried out for 15 minutes. After reaction termination, after removing muddiness of a minute amount by filtration actuation, toluene was distilled off by the rotary evaporator and 10.8g of wax-like polymers was obtained. Yield was 87%. The GPC analysis result of this polymer is shown in drawing 9. The number average molecular weight Mn of this polymer by polystyrene conversion was 810, and n was an average of 4.95. Moreover, weight average molecular weight

Mw was 1,474, and degree of dispersion (Mw/Mn) of a polymer was 1.92. Next, the proton nuclear-magnetic-resonance spectrum ( $^1\text{H-NMR}$ ) of this polymer is shown in drawing 10. The peak (integral value: 200.73) of the proton combined with the internal double bond is observed at the peak (integral value: 19.99) based on the end olefin of Ha and Hb of the following formula, and 5.21–6.00 ppm at the peak (integral value: 32.18) of a methyl group based on 3-ethyl oxetane structure to 0.83–0.95 ppm, and 4.90–5.08 ppm. By analyzing this result, an oxetane radical exists in the piece end of a polymer, and it is checked that n of the following type is the polymer of 4.8.

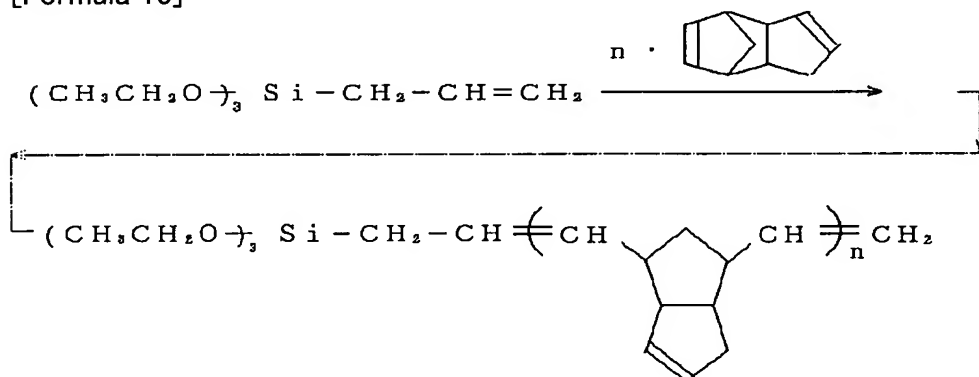
[0042]

[Formula 18]



[0043] Composition of an example 6 triethoxysilane end polymer [0044]

[Formula 19]



a thermometer and electromagnetism -- toluene 13.12g, dicyclopentadiene of 99% of purity 10.02g (75.8mmol), and allyl compound triethoxysilane 3.11g (15.2mmol) were taught to 100ml 3 Thu opening flask which attached the rotator, and it agitated at the room temperature (25 degrees C) (mole-ratio = a [dicyclopentadiene] / [allyl compound triethoxysilane] = 4.98, substrate concentration = 50.0%), and considered as the homogeneity solution. 42.0mg (it is the 0.419 weight section to 5.10x10 to 5 mol and the dicyclopentadiene 100 weight section) was added for the screw (tri-cyclohexyl phosphine) Ben Jiri Jean ruthenium dichloride shown by the formula (a) as a catalyst to this. While adding the catalyst, the temperature in a flask rose, and it amounted to 60 degrees C after [ of reaction initiation ] 4 minutes. The temperature in a flask fell gradually after this, and the inside of a flask became 27 degrees C in 50 minutes after reaction initiation. At this time, 1.05g (12.2mmol) of acetic-acid vinyl ester was added, and churning was carried out for 15 minutes. After reaction termination, after removing muddiness of a minute amount by filtration actuation, toluene was distilled off by the rotary evaporator and 12.1g of wax-like polymers was obtained. Yield was 92%. The GPC analysis result of this polymer is shown in drawing 11. The number average molecular weight Mn of this polymer by polystyrene conversion was 1,056, and n was an average of 6.44. Moreover, weight average molecular weight Mw was 1,550, and degree of dispersion (Mw/Mn) of a polymer was 1.47. Next, the proton nuclear-magnetic-resonance spectrum ( $^1\text{H-NMR}$ ) of this polymer is shown in drawing 12. The peak (integral value: 130.88) of the proton combined with the internal double bond is observed at the peak (integral value: 12.83) based on the end olefin of Ha and Hb of the following formula, and 5.20–6.00 ppm at the peak (integral value: 28.92) of a methyl group based on triethoxysilane to 3.75–3.93 ppm, and 4.90–5.07 ppm. analyzing this result -- the piece end of a polymer -- TORIE -- an ibis -- a silane radical exists and it is checked that n of the following formula is the polymer of 4.9.

[0045]

[Formula 20]

[Effect of the Invention] The metathesis ring-opening-polymerization object of the dicyclopentadiene by which it has the functional group of this invention at the piece end, and molecular weight was controlled is an ingredient useful to the property improvement of the polymer ingredient of various kinds [ have / functions, such as reactivity, radical polymerization nature, fire retardancy, and an adhesive property to various base materials, ], and the improvement in the engine performance.

[Translation done.]

\* NOTICES \*

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.\*\*\*\* shows the word which can not be translated.

3.In the drawings, any words are not translated.

---

DESCRIPTION OF DRAWINGS

---

[Brief Description of the Drawings]

[Drawing 1] The GPC chart of the polymer obtained in the example 1

[Drawing 2] Polymer obtained in the example 1 <sup>1</sup> H-NMR spectrum

[Drawing 3] The GPC chart of the polymer obtained in the example 2

[Drawing 4] Polymer obtained in the example 2 <sup>1</sup> H-NMR spectrum

[Drawing 5] The GPC chart of the polymer obtained in the example 3

[Drawing 6] Polymer obtained in the example 3 <sup>1</sup> H-NMR spectrum

[Drawing 7] The GPC chart of the polymer obtained in the example 4

[Drawing 8] Polymer obtained in the example 4 <sup>1</sup> H-NMR spectrum

[Drawing 9] The GPC chart of the polymer obtained in the example 5

[Drawing 10] Polymer obtained in the example 5 <sup>1</sup> H-NMR spectrum

[Drawing 11] The GPC chart of the polymer obtained in the example 6

[Drawing 12] Polymer obtained in the example 6 <sup>1</sup> H-NMR spectrum

---

[Translation done.]



## \* NOTICES \*

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

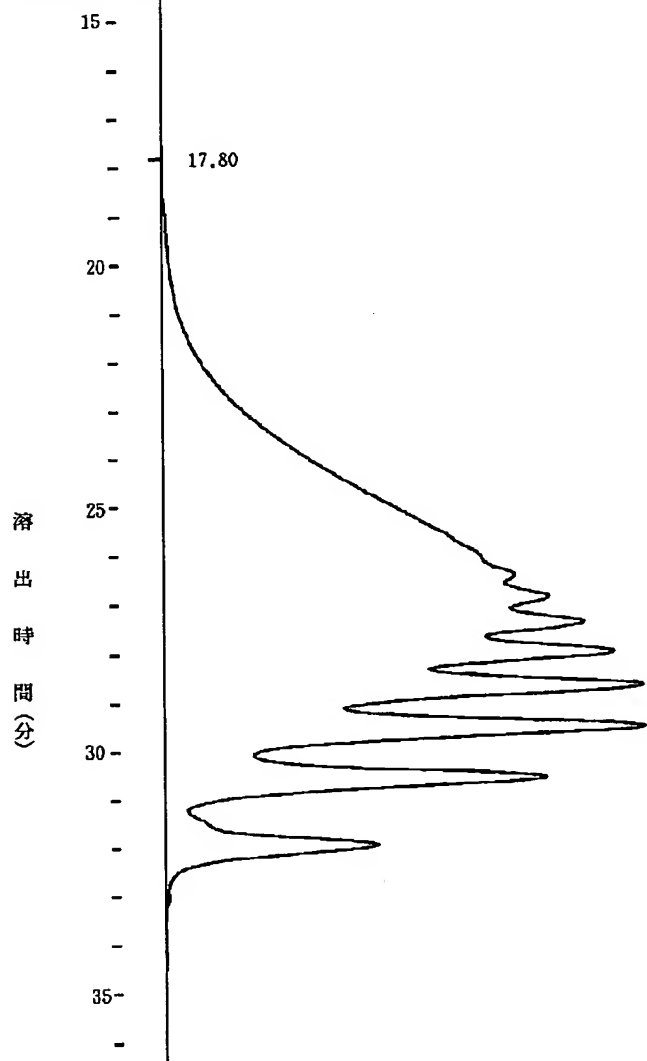
1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.\*\*\*\* shows the word which can not be translated.

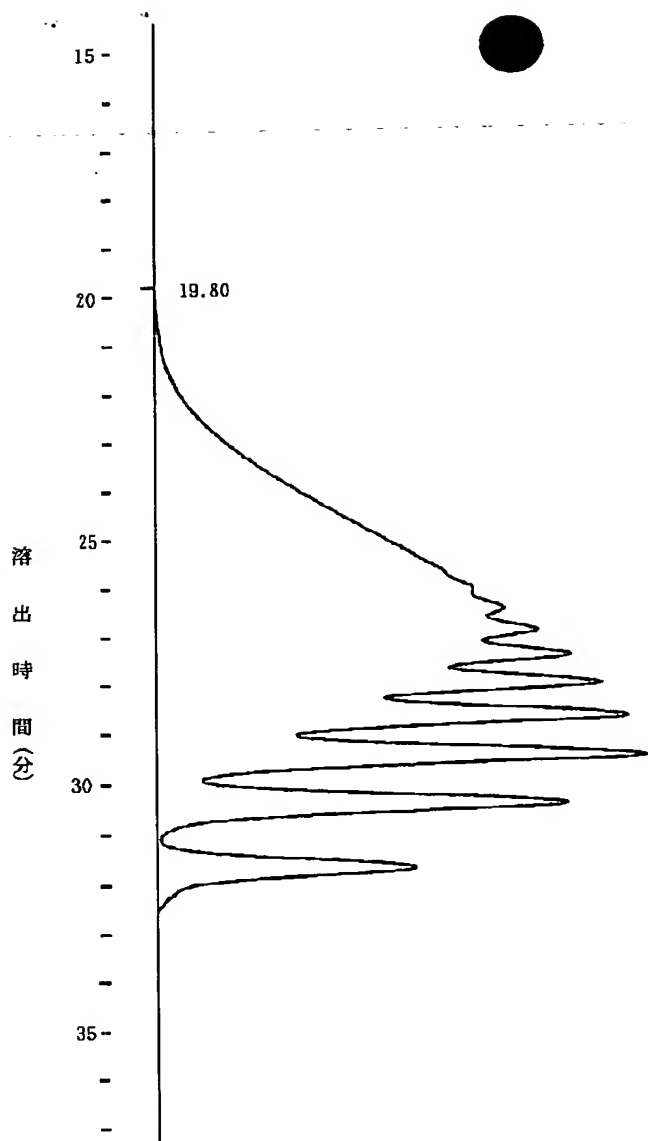
3.In the drawings, any words are not translated.

## DRAWINGS

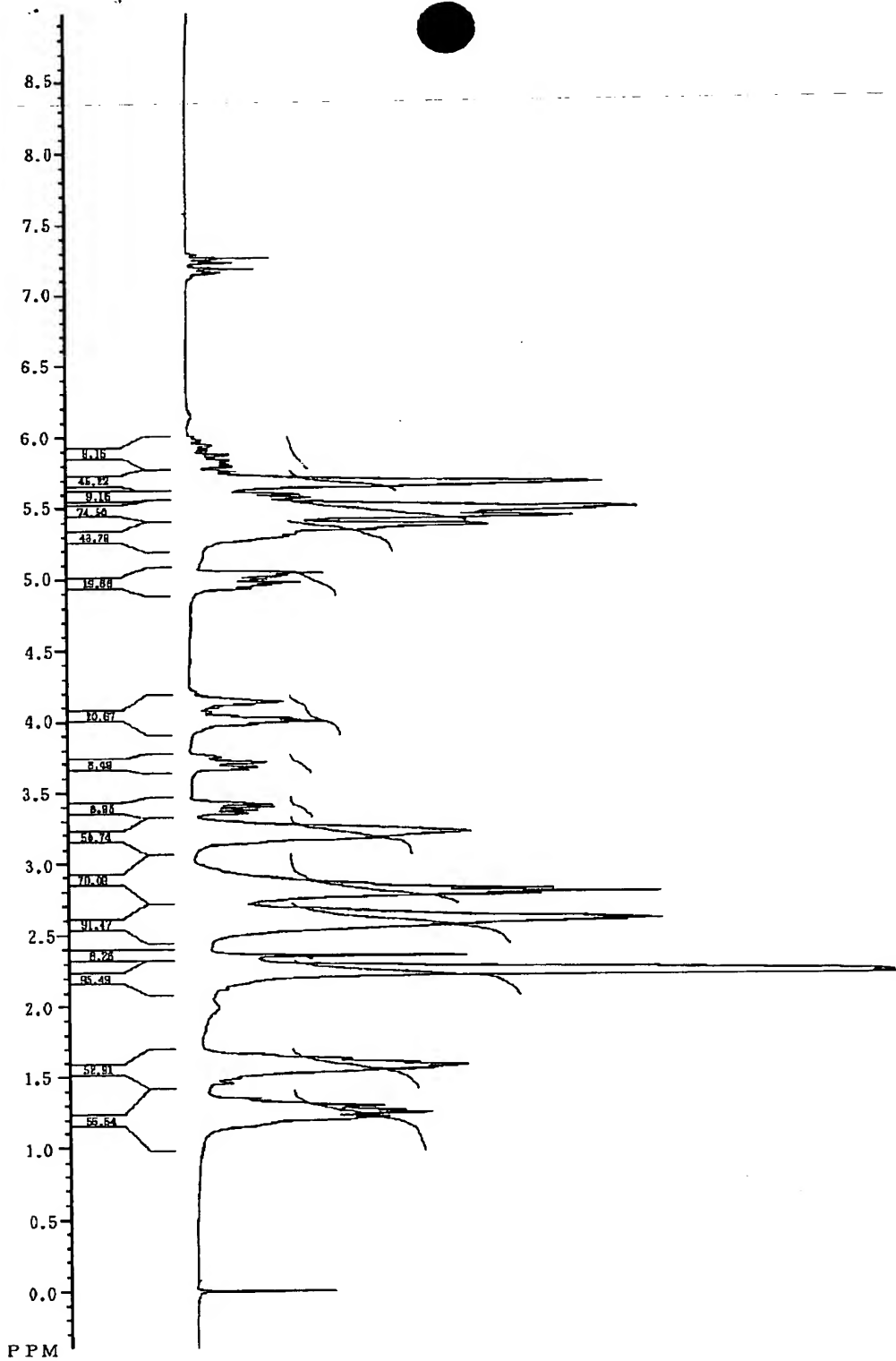
[Drawing 1]



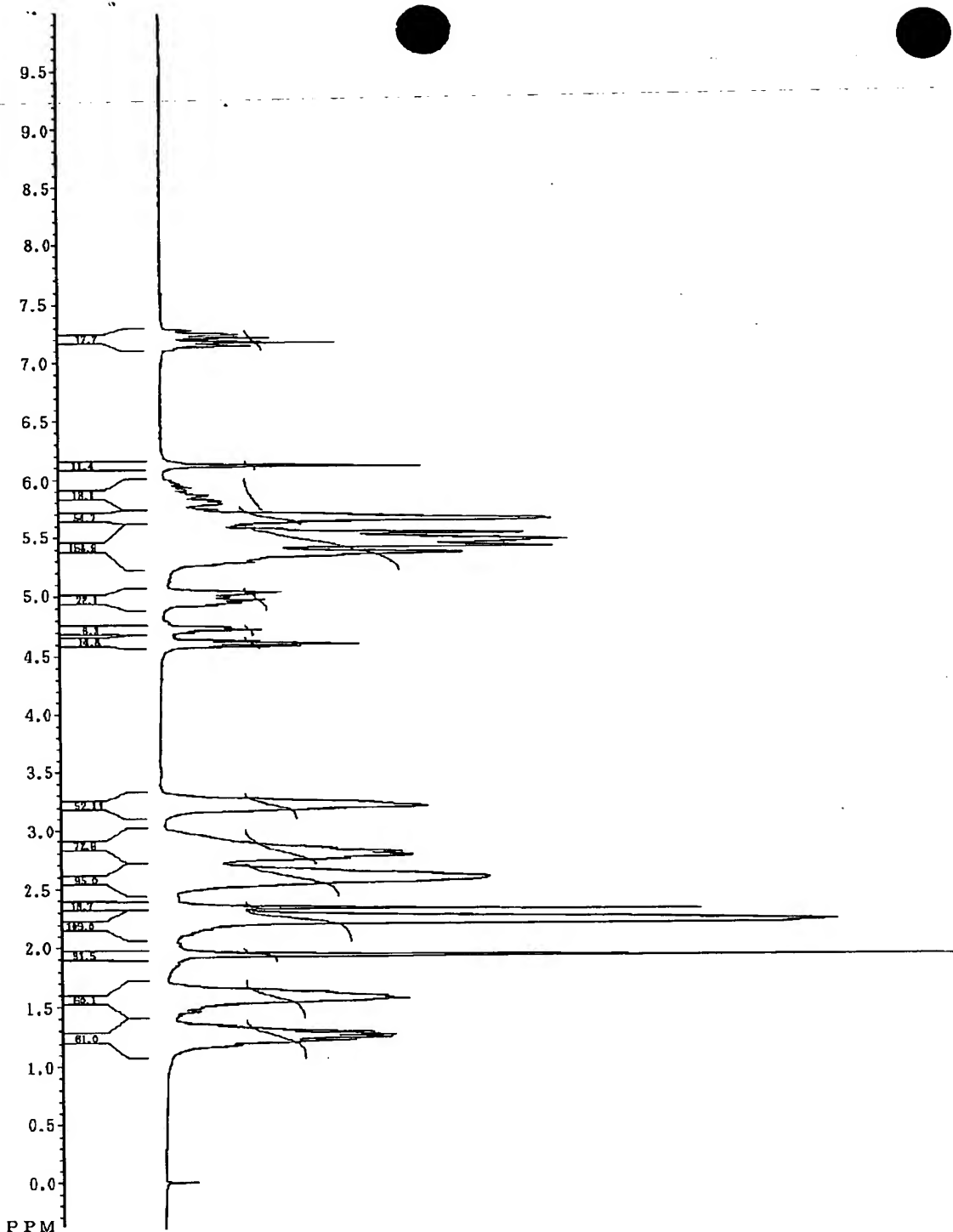
[Drawing 3]



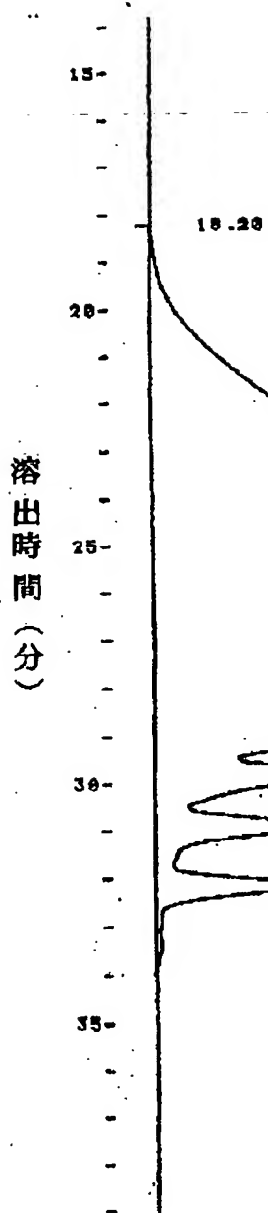
[Drawing 2]



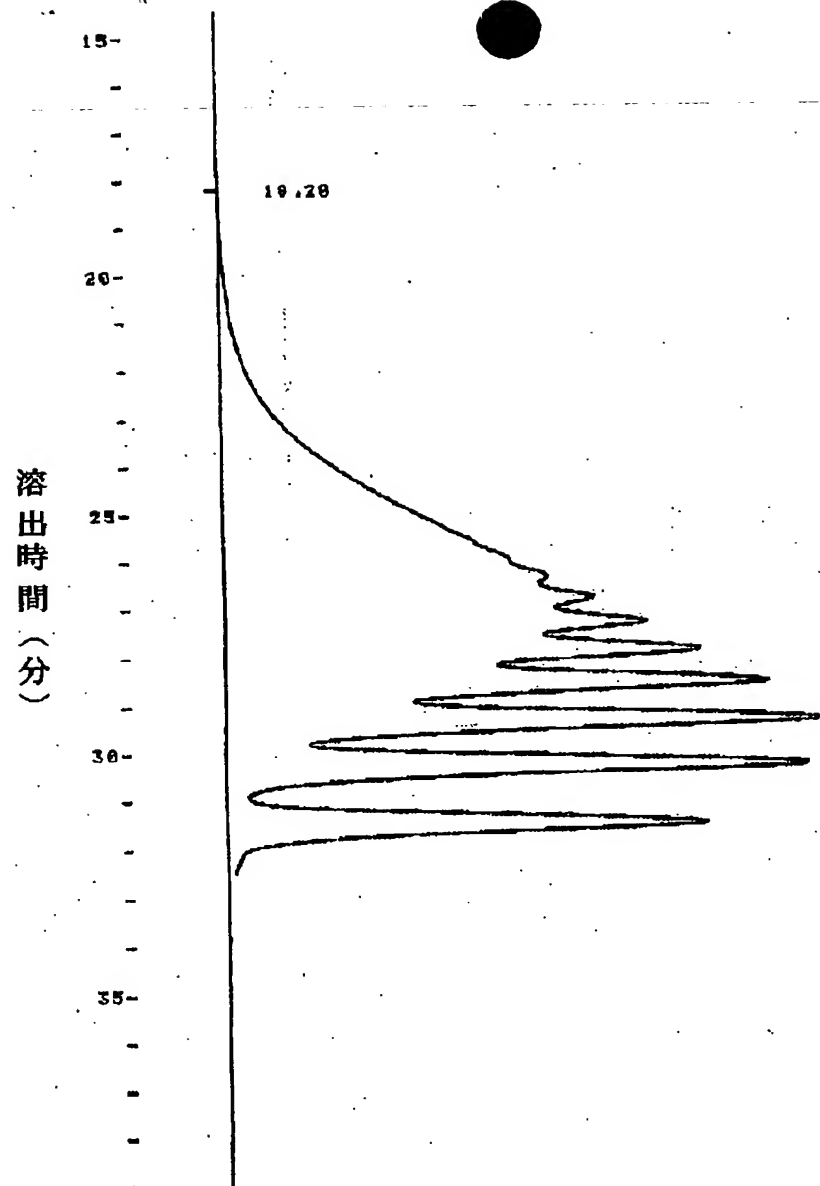
[Drawing 4]



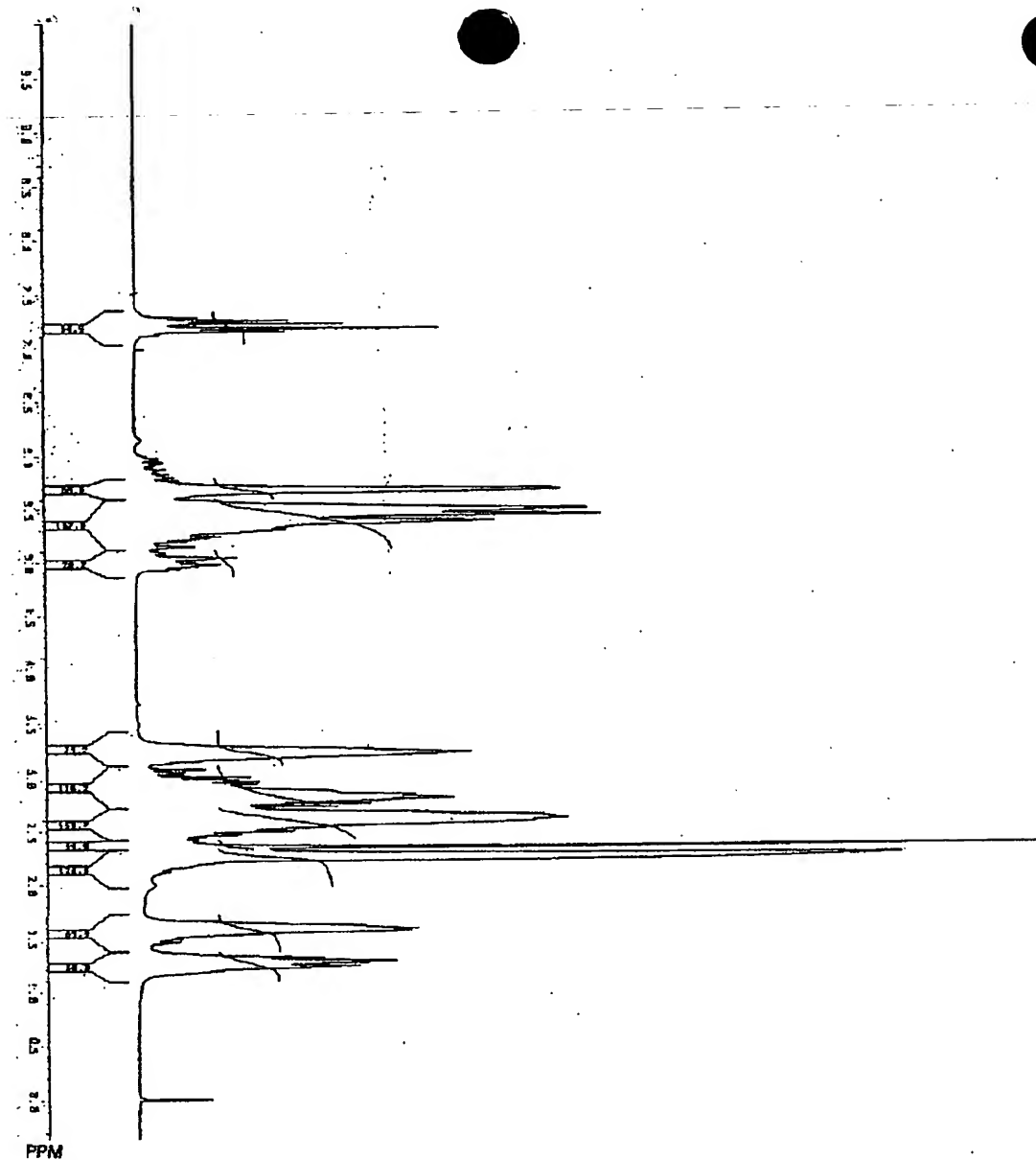
[Drawing 5]



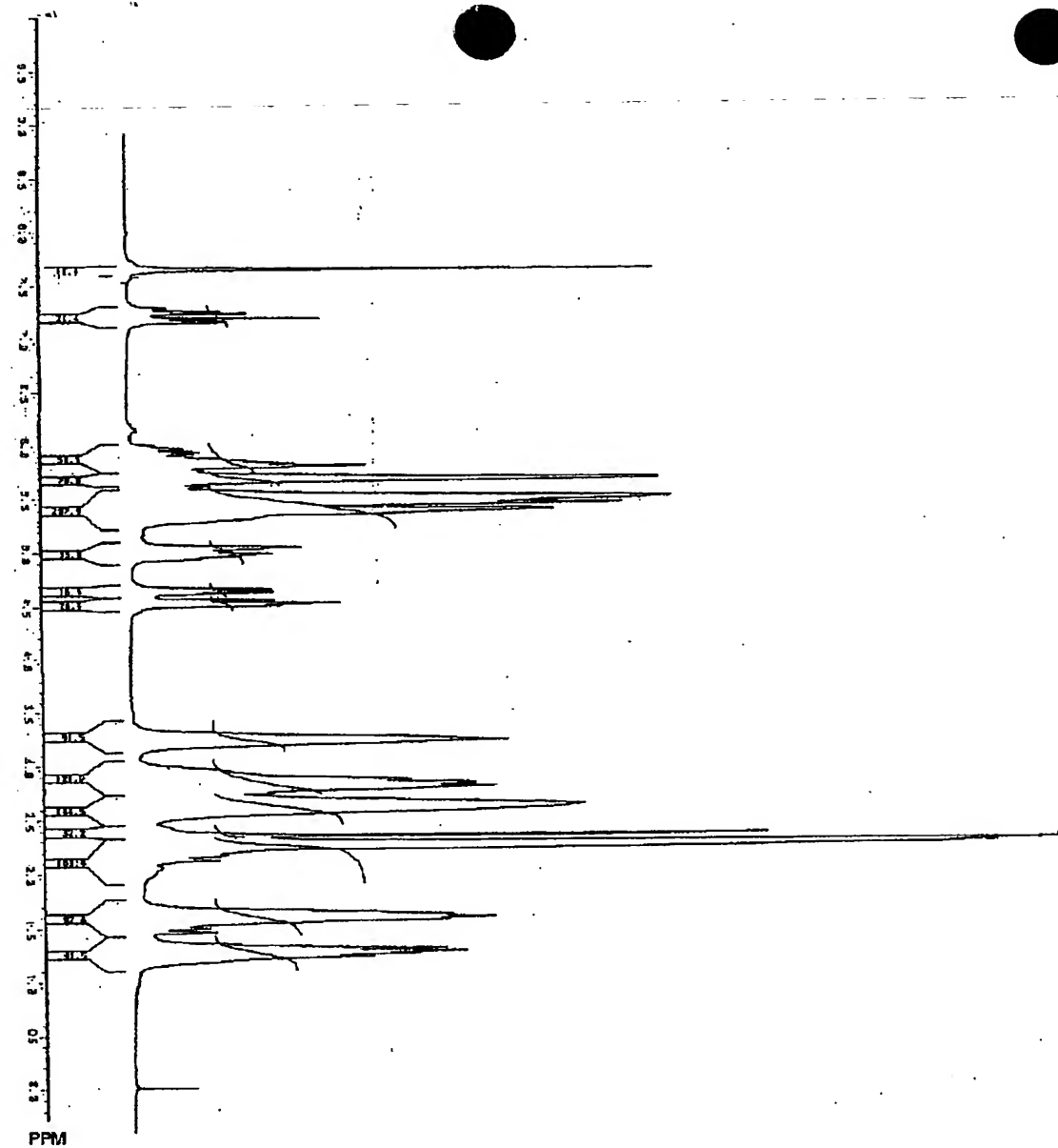
[Drawing 7]



[Drawing 6]



[Drawing 8]



[Drawing 9]



溶出時間 (分)

15-

20-

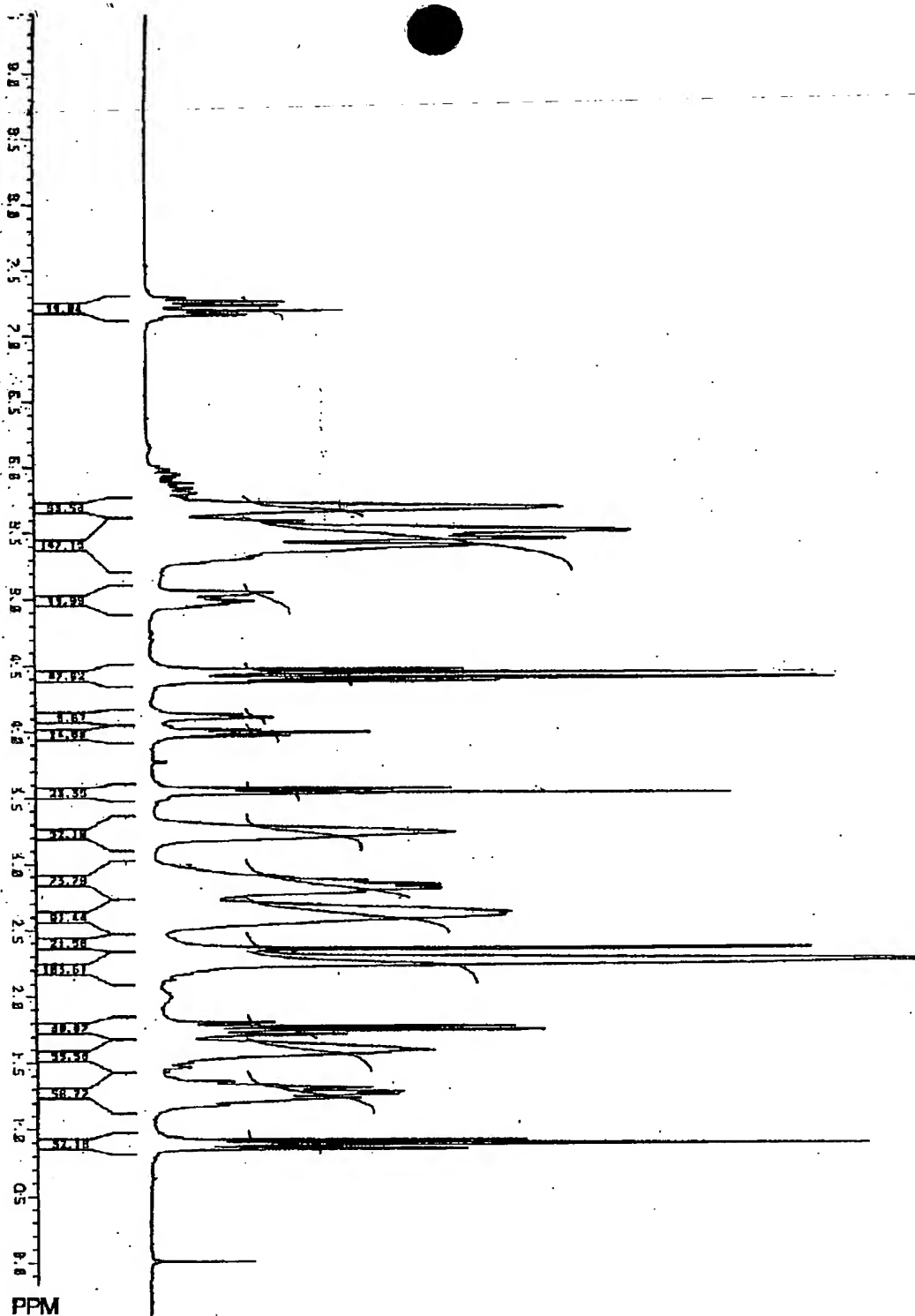
25-

30-

35-

20.20

[Drawing 10]



[Drawing 11]

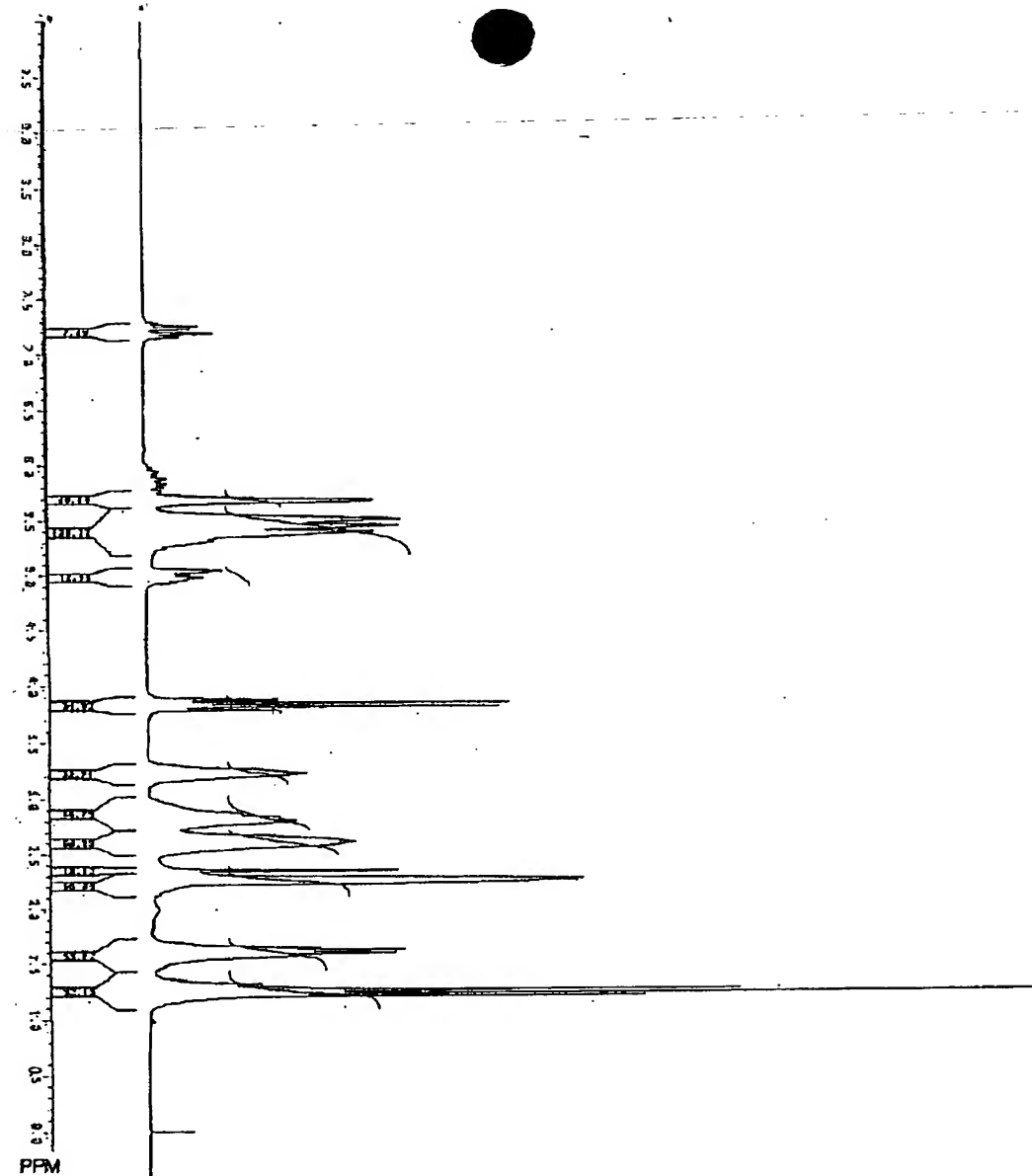
溶出時間 (分)

20.20

30-

35-

[Drawing 12]



[Translation done.]

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

☐ BLACK BORDERS

☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES

☐ ~~FADED~~ TEXT OR DRAWING

☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING

☐ SKEWED/SLANTED IMAGES

☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS

☐ ~~GRAY~~ SCALE DOCUMENTS

☒ LINES OR MARKS ON ORIGINAL DOCUMENT

☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY

☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**